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VIII.

THE LATENT HEAT OF EVAPORATION OF STEAM FROM SATURATED SALT SOLUTIONS.

By FREDERICK T. TROUTON, Sc.D., F.R.S.

[Read November 30, 1899.]

In the first part of this Paper is described an apparatus which I have employed for determining the latent heat of evaporation of steam from saturated salt solutions, as well as some results obtained therewith. In the second part are considered the circumstances connecting this with the latent heat of solutions of the salt. In the third part an apparatus is described for determining the cooling consequent on dissolving the salt in water at temperatures above the boiling point.

PART I.

In determining the latent heat of evaporation from saturated solutions, recourse must be had to a method in which heat is supplied to effect the evaporation, instead of employing one of the more usual condensation methods.

The apparatus used is a modified form of that shown some time since at the Dublin University Experimental Science Association,* and is very similar to that so successfully used by Miss Dorothy Marshall and Professor Ramsay.†

Description of Apparatus.

The solution to be evaporated is placed in a cylindrical vessel, itself completely immersed in an outside vessel containing the same solution. The outside vessel is kept boiling throughout the experiment, and is consequently at approximately the same temperature as the liquid in the inner vessel; so that no sensible quantity of heat can pass either out from or into the inner vessel. The heat, to effect evaporation in the inner vessel, is

* *Nature*, vol. xxx. (1884), p. 187. † Phil. Mag., vol. xli. (1896), p. 38.

provided by an electric current, which is passed through a platinum spiral contained in a metallic case immersed in the inner vessel. The steam thus produced passes out through a side tube, is condensed and weighed.

A second apparatus, similar to this, but containing pure water, had the same current passed in series through its spiral, which was made to have about the same resistance as the other spiral. The exact ratio between the two resistances was found in each experiment by the deflection of a high resistance galvanometer, applied in turn as a shunt to the resistances.

From this ratio, and from the ratio of the weights of steam condensed from the pure water and from the solution, the latent heat of the latter is got, in terms of that of pure water.

The apparatus (fig. 1) was made of copper, and so arranged as to be capable of being taken to pieces. In this way, after an experiment, the solid residue of precipitated salt could be easily removed. The inner vessel was ultimately made with double walls, enclosing an air-space between, in order to diminish any possible transference of heat; for it was found difficult, when dealing with solutions, to prevent a slight difference in temperature between outside and inside, depending on the rate the evaporation was proceeding at.* Thermometers were provided to enable this to be observed, and, as far as possible, corrected, by altering the intensity of the flame under the outside vessel. The water evaporated from the outside vessel was condensed and returned so as to keep the level constant.

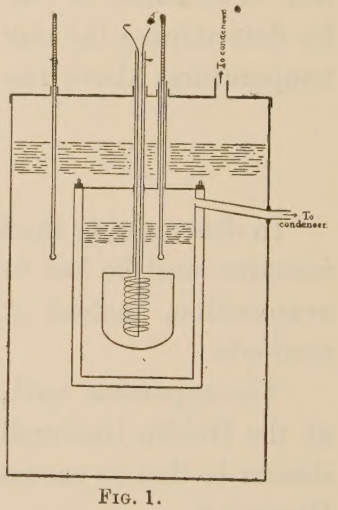

FIG. 1.

The inside vessel was supported by two arms, and by the delivery tube acting as a third. This last was made to screw together where it passed through the outside vessel. The other two supports rested in sockets attached to the outer vessel. The top of the inner vessel was clamped down with four nuts. It carried two tubes reaching to above the top of

* In order to admit of complete immersion, the pressure height at corresponding levels inside and outside must necessarily be different, and consequently the temperature also.

the outside vessel. One of these was for a thermometer, the other for bringing in the insulated leads for the current, and was made air-tight. This tube ended in a closed vessel or case, which contained the platinum spiral. This was wound on an asbestos core to prevent sagging of the coils when hot, and their possibly touching together with, as a result, an alteration of the resistance.

Testing of the Apparatus.

Some experiments were made with water in both calorimeters to test how far the results might be relied on. These are given in Table I. W_1 and W_2 are the weights of condensed water collected from the two calorimeters during the same time; E_1/E_2 gives the mean ratio of the electromotive forces acting on the spirals of the two calorimeters. In the fourth are given the ratio of W_1/W_2 in each case, for the sake of comparison.

TABLE I.

W_1.	W_2.	E_1/E_2.	W_1/W_2.
9·28	8·88	1·048	1·045
7·25	6·85	1·053	1·058
7·32	6·95	1·047	1·053
9·78	9·32	1·036	1·042

Apparently, from this Table, individual results might be relied on to 1 per cent.; but against this it may be mentioned that experiments with water in both calorimeters are much more easily made than with saturated solutions. With these at the beginning of an experiment there was always a danger lest heat should pass inwards, while towards the end the danger was the other way. This latter through a solid bridge of deposited salt forming across from the heater containing the spiral to the walls and bottom of the inner vessel. This solid mass might obviously rise to a temperature considerably higher than that of the solution, and thereby possibly cause a loss by heat passing to the outer vessel. A gain in heat

from the outside at the beginning often arose from commencing to collect the condensed steam before the temperature of the inner vessel reached its maximum throughout. The apparatus was always charged with a solution saturated, and as hot as possible; but the temperature necessarily fell to somewhat under the maximum during the process, with accordingly a loss of salt by precipitation, so that, until a certain amount of steam had been driven off, the boiling point would be below its maximum. Care had to be taken that the collection of condensed steam was only made between these two limits.

Results with Sodium Nitrate and Sodium Sulphate.

In the following Tables are given the results obtained with solution of sodium nitrate, boiling at about 121°, and of sodium sulphate, boiling at about 103·5°.

In the first column are given the weights condensed from the calorimeter containing water alone; in the second the weight got from the salt solution; in the third column the ratio of the electromotive forces; and in the last the latent heat calculated by means of these from the equation

$$\lambda W_s / 537\, W = E_s / E.$$

TABLE II.

W.	W_s.	E/E_s.	λ.	W.	W_s.	E/E_s.	λ.
19·26	20·90	1·048	472·2	52·89	58·37	1·036	469·6
33·85	35·83	1·048	483·9	40·63	45·36	1·028	467·9
24·96	26·60	1·041	484·0	9·62	10·43	1·020	485·6
41·29	45·69	1·039	467·0	26·41	27·95	1·028	493·6
37·88	40·96	1·039	477·9	26·89	28·70	1·028	489·4
40·39	42·65	1·040	488·9	16·00	18·16	1·012	467·5
30·94	34·21	1·036	468·8	24·28	26·71	1·017	480·0
				Mean, .		$\lambda = 478·3$.	

The "probable error" in this result comes out to be about ·3 per cent.

TABLE III.

Sodium Sulphate.

W.	W_s.	E/E_s.	λ.
10·27	9·99	1·07	515
15·51	14·49	1·06	542
13·11	12·63	1·05	531
Mean, . . $\lambda = 529$.			

The probable error in this case is about 1 per cent. Further experiments were not made, as it was found that the solution injured the calorimeter. Also the alteration in hydration which takes place renders it a difficult salt to work with.

Results with Calcium Chloride.

Experiments were also made with commercial calcium chloride (so-called), a substance which does not produce with water a solution having a maximum boiling point of the same character as that of the two bodies dealt with above. If its solution is boiled, as it loses water the temperature continually rises until a point is reached when the mass becomes solid throughout, there being no point at which a solid precipitate separates out, leaving a solution of constant density. This distinction may very possibly be connected with the fact that heat is given out when this substance goes into solution, while with the two others heat is absorbed. This substance and sodium nitrate may be taken each as the type of a distinct class. As such they were selected for the purposes of this investigation. When the latent heat is measured, as it necessarily must be with the calcium chloride solution, at temperatures other than a maximum, the determination

is complicated by the temperature rising during the operation, thereby making a correction necessary for the heat required to effect this.

Determinations were made at three different temperatures with solutions of different strengths, at about 103° and about 120°, and about 140°. In the first column in Table IV. are given the temperatures each experiment began at. According as steam came off the temperature rose; the value of this at the end is given in the second column. The others mean the same as before.

Though every endeavour was made that the outside vessel should rise in temperature at the same rate as the inside by allowing more or less steam to escape from it without being returned on condensation, nevertheless there were generally small differences between the temperature inside and out throughout every experiment. These results must therefore be considered as less reliable than those obtained with substances possessing a definite boiling point.

To estimate the proportion of the total heat supplied by the current which went to raise the temperature of the solution is comparatively easy, given V the volume of the solution contained in the inner vessel, its density δ and its specific heat S; but it is difficult to say how much of the inner vessel itself was heated from within and how much from outside. The heating of one-third its weight was thought to be about the probable proportion to be credited to inside. Were the heating of even the entire vessel attributed to inside, it would affect the final result by only about $\frac{1}{2}$ per cent. Let C be the weight of the inner vessel and S' its specific heat, then taking the latent heat of steam to be 537, we have, for obtaining λ, the latent heat of the steam from the solution,

$$\lambda W_s + (V\delta S + 1/3\ CS')(\theta_1 - \theta_2) = 537\ WE_s/E.$$

TABLE IV.

θ_1.	θ_2.	W.	W_s.	E/E_s.	λ.	
140·0	142·5	20·25	15·50	1·00	651	
144·0	145·0	10·18	6·82	1·00	746	
139·0	141·0	19·06	13·91	1·00	685	Mean, 683
141·0	143·0	15·02	10·61	1·03	671	
142·3	143·7	18·60	9·81	1·02	678	
119·0	120·2	23·16	19·87	1·02	592	
120·7	122·2	25·84	21·29	1·01	621	Mean, 606
101·7	101·9	34·83	30·40	1·13	542	
101·6	101·6	21·91	19·91	1·06	548	Mean, 545

These three values, at the different temperatures as far as they go, point to the latent heat being a linear function of the temperature. This, it will be remembered, is also the case when the temperature of boiling of water is also altered by altering the pressure instead of, as here, by the addition of salt.

It will be noted that, unlike in the case of the previous salts, the latent heat is greater than that of steam from water alone. This, no doubt, depends on the fact that heat is generated when calcium chloride dissolves in water, while the other salts produce a lowering in temperature.

PART II.

When a liquid is evaporated containing a salt in solution, the latent heat will, in general, differ from that of the pure solvent; and a diminution or increase in amount over the latent heat of pure water is to be looked for according as heat is absorbed or

given out when the salt is dissolved. The amount of this alteration should apparently be ascertainable by the principle of equivalents from the latent heat of solution of the salt. This has been tested in the case of sodium nitrate in the way described below, but the calculated result is at complete variance with the experiments.

As perhaps affording an explanation of the cause of this disagreement it is to be remarked that the latent heat of solution which is dealt with in the calculation is that necessary to prevent a change in temperature occurring on solution taking place, whereas that actually found (Part III.) by experiment necessarily depends on allowing a fall in temperature, on mixing the bodies together, to take place.

In consequence of this an endeavour was made to construct a reversible thermo-dynamic cycle, which would give the cooling under the actual circumstances of the experiments (Part III.). The calculated value in this case agrees very satisfactorily with the experiments.

The Latent Heat of Solution of Saturation.

Suppose a saturated solution of the salt containing one gram of water to be under a piston in a cylinder at the pressure P_1. Let heat λ be supplied to evaporate to dryness at constant pressure. The solution increases from v_1 to V_1. Let the salt and steam be separated by a partition, and let the steam be compressed at constant temperature to saturation at volume V_2, giving out heat Q in amount. Let the steam now condense, giving out heat λ_1 at constant pressure P_2. Finally, withdraw the partition, so as to allow solution to take place at constant temperature, the necessary heat L being supplied. We have approximately, then, from the principle of equivalence,

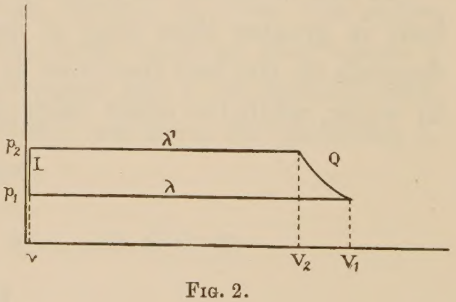

FIG. 2.

$$L = \lambda - \lambda_1 + \left[Q + \int_{V_1}^{V_2} p dv \right] + P_2 (V_2 - v_2) - P_1 (V_1 - v_1).$$

Applying this to the case of sodium nitrate, we have

$\lambda = 478{\cdot}3$. (Part I.)

$\lambda_1 = 512{\cdot}5$. (The latent heat of steam at 121°, the boiling point of the saturation solution.)

$P_2 = 2093$ gr./sq. c. (The pressure of saturation steam at 121°.)

$P_1 = 1033$ gr./sq. c.

$V_2 = 979$
$V_1 = 1724$ } (Deduced from Landholt and Bornstein's Tables.)

v_1 and v_2 may both be assumed to be equal to 1 c. c.

Were Boyle's law assumed to hold, the sum of the third and fourth terms on the right-hand side would vanish. In any case their effect must be small.* Neglecting this, we get for the value of the latent heat of solution, $L = 37$ about.

Now the value deduced from experiments detailed in Part III., made by observing *the fall in temperature* on mixing, is $L = 83$. Under these circumstances it seemed desirable, as mentioned before, to have a method of calculation which would directly give the fall in temperature on mixing at a given temperature, thus avoiding all uncertainty on this point. With this view the following method is given, in which, by the assumption of a semi-permeable membrane† it is possible to construct a cycle of operations which is reversible, and which avoids uncertainty arising from any possible variation of the latent heat of solution with temperature.

Construction of a Reversible Cycle.

The cycle is shortly as follows:—The saturated solution is first supplied with heat to evaporate to dryness. Next the temperature is raised by

* Assuming Van der Waal's equation, an expression was deduced by the employment of which the effect of these terms on L was found to be about one unit.

† The semi-permeable membrane here required would, no doubt, have to possess properties perfect to a degree beyond anything our actual experience warrants. This of itself need not invalidate an argument otherwise consonant with facts any more than the assumption of an adiathermous substance does.

compression the proper amount, and the vapour further isothermally brought to saturation. Next the vapour is allowed to condense, giving out heat, the amount of which is known, for it is the latent heat of the pure solvent. Then, to complete the cycle, the salt has to be allowed to dissolve in the solvent, now condensed to the liquid state, but this must be done in such a way that the step is reversible. This necessitates the use of a semi-permeable membrane, which we may suppose arranged as follows:—Let a perfectly non-conducting cylinder be filled with a saturated solution, and let it be fitted with a kind of double piston or rather two pistons, the inner one being made of a semi-permeable membrane. To effect the separation of the salt and solvent, when going round the cycle in reverse order a force is applied to the inner piston so as to raise the pressure of the solution to just above the osmotic pressure. This is continued till all the solvent is separated out between the pistons. Going round the cycle in the direct order, we now see that the solution of the salt must take place by the solvent passing through the semi-permeable membrane. To effect this the pressure is to be kept beneath the semi-permeable piston at slightly less than the osmotic pressure.

It will have been observed that, in this cycle, heat is given out or taken in only at two definite temperatures—the range in temperature through which the salt and solvent pass on solution being allowed to take place as described. We know the amount of heat given out on the compression and liquefaction of the vapour, so that we can get at once a relation connecting the latent heat of evaporation of the solution with the change in temperature accompanying solution under the osmotic condition specified.

Details of the Cycle.

To go more minutely into the details of the cycle, let us suppose a quantity of the saturated solution to be taken at the boiling point containing unit weight of solvent, and let the boiling point be T_1 under the pressure P, and let the latent heat of evaporation be λ_1. Then the four

stages (fig. 3) are as follows:—(1) In the first a quantity of heat λ_1 is supplied at the temperature T_1, to evaporate to dryness. (2) In the second stage, the dry salt and vapour are separated by a perfectly conducting partition, and adiabatically compressed in such a way that the temperature at any moment throughout the mass of salt and vapour is the same. The temperature is thus raised to T_2—which will be specified later. (3) The third stage is in two parts. In the first, compression is continued but isothermally till saturation is reached, the necessary heat Q being meanwhile removed. In the second part, the vapour condenses at constant pressure, giving out a quantity of heat λ_2, the latent heat of the pure solvent at the temperature T_2. (4) In the fourth stage, the liquid combines with the salt on passing through a semi-permeable diaphragm under the conditions necessary to admit of reversibility. A fall in temperature results. The temperature can now be defined as such that the liquid, on the solution being completed, comes back to the initial temperature T_1.

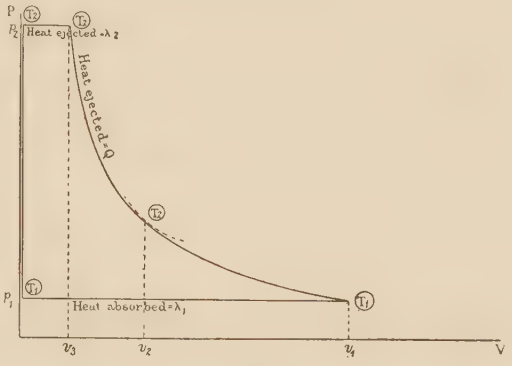

FIG. 3.

Since no heat is taken in or given out throughout the cycle except at the temperature T_1 and T_2, we have

$$(\lambda_2 + Q)/\lambda_1 = T_2/T_1.$$

Both λ_2 and Q are known functions of T_2, so that if say λ_1 has been observed, we can deduce the value of $(T_2 - T_1)$, the fall in temperature which occurs on the salt going into solution: the solvent having, however, to pass through a semi-permeable diaphragm in the way explained.

Comparison with Thermal data.

There can be, of course, no direct experimental data of the cooling which takes place when a salt goes into solution under these circumstances; but it can only differ from that on ordinary solution taking place by a

small amount due to the work done by the osmotic forces. To calculate this we require to make some estimate of the probable value of the osmotic pressure, let this be P_3. In stage (4) the semi-permeable piston traverses a volume equal to that of one gramme of the solvent. On the back of this piston the pressure is P_2, so that the work done is $(P_3 - P_2)/D_2$, where D_2 is the density of the solvent at the temperature T_2 and pressure P_2. A small amount of work is done by the other piston, and also at the end of the operation when the pressure is reduced to P_2; but these are comparatively small, and may be neglected. If T_1' be the temperature to which the solution would fall if it were dissolved in the ordinary way, we can say then

$$(T_2 - T_1) = (T_2 - T_1') + (P_3 - P_2)/JWSD_2$$

where J is Joule's equivalent, W the weight of solution containing unit weight of solvent, and S the specific heat of the solution.

Case of Sodium Nitrate.

The fall in temperature $(T_2 - T_1')$ was calculated in the case of sodium nitrate and water from the value given in Part I. for the latent heat of evaporation. The details of the calculation are given below. The value found (a fall of over 40°) agrees satisfactorily with that observed and detailed in Part III.

Calculations of the fall in Temperature on mixing of the dry Salt and Water.

In order to find T_2 the upper temperature in the cycle, we must be able to express λ_2 and Q in terms of T_2 in the expression $(\lambda_2 + Q)/\lambda_1 = T_2/T_1$. The latent heat λ_1 of the saturated solution and its boiling point T_1 we supposed known. For λ_2, the latent heat of steam from pure water at the temperature T_2, we can say, using Regnault's formula expressed in absolute temperatures, $\lambda_2 = 796{\cdot}2 - {\cdot}695\ T_2$. For Q we have $Q = \int_{v_3}^{v_2} p dv$ where

v_2 and v_3 are the volumes at the beginning and end of the isothermal compression in part (3) of the cycle.

Value of the Constants for Steam in Van der Waal's Equation.

In order to best get the value of these volumes recourse was had to Van der Waal's equation

$$\left(p + \frac{a}{v_2}\right)(v - b) = RT.$$

For this purpose the value of the constants for steam had first to be calculated, as they could not be found to hand. They are as follows where v is in cubic centimetres, and p is in centimetres of mercury. They were calculated from data given in Landholt and Bornstein's Tables for temperatures 180° and 140°.

$$a = 8{\cdot}9 \times 10^6, \quad b = 33{\cdot}45, \quad R = 345{\cdot}5.$$

Evaluation of the limits in $Q = \int_{v_3}^{v_2} p\,dv.$

To get v_2 we have, as the condition for the adiabatic compression in stage (3), $p\,dv + (ws + c)\,dT = 0$, where w is the weight of dry salt, and s its specific heat, and c the specific heat of steam at constant volume. Substituting for p from Van der Waal's equation, and neglecting the effect of the compressibility of the salt, we can get

$$\int_{v_1}^{v_2}\left(\frac{R}{v - b} - \frac{a}{Tv^2}\right)dv = -\int_{T_1}^{T_2}\frac{(ws + c)}{n}\frac{dT}{T},$$

where $$n = 13{\cdot}59 \times 981/41{\cdot}6 \times 10^6.$$

Now v_1 the volume of steam before the adiabatic compression begins is known. It can be found from Van der Waal's equation by putting

in the atmospheric pressure and the temperature of the boiling point. Therefore we can get v_2 on integrating, which may be done by inserting in the second term, which is small compared to the first, the approximate value

$$T = T_1 \frac{(v_1 - b)}{(v - b)} \frac{nR}{sw + c}$$

found by neglecting a. Thus we get after expanding

$$R \log\left(\frac{v_1 - b}{v_2 - b}\right) - \frac{a}{T_1(v_1 - b)} \left\{\frac{1}{q-1}(v_1^{q-1} - v_2^{q-1}) - \frac{b}{q-2}(v_1^{q-2} - v_2^{q-2}) + \&c.\right\} = \frac{ws + c}{n} \log \frac{T_2}{T_1}$$

where $q = \dfrac{nR}{ws + c}$. In making the calculation in any particular case some assumed value of T_2 can be taken, and the corresponding value of v_2 found from this. The other limit v_3 presents no difficulty. It can be found from tables of saturated steam for the given temperature T_2.

Completion of the Calculation.

On substituting for p from Van der Waal's equation in $Q = \int_{v_2}^{v_3} p dv$, and integrating, we have

$$Q = nR\ T \log \frac{v_2 - b}{v_3 - b} + na\left(\frac{1}{v_2} - \frac{1}{v_3}\right).$$

If the right value for T_2 has been assumed, the value of Q thus found added to λ_2 should be to λ_1 in the ratio of T_2 to T_1. A few trials will suffice to enable the right value to be ascertained. The fall in temperature $T_2 - T_1$ is that taking place under the osmotic condition necessary for reversibility; but, as explained above, if we subtract the temperature fall equivalent to the external work done during the osmotic transformation, we can arrive at the fall consequent on simply mixing the dry salt with water in the ordinary way.

Data used in the case of Sodium Nitrate.

The numerical data used in the calculation for sodium nitrate are as follows:—

The heat evaporation of the salt solution, . .	$\lambda = 478{\cdot}3$
Temperature of the boiling point (121°), . .	$T_1 = 394{\cdot}0$
Weight of salt to one gramme of water in the saturated solution, ...	$w = 2{\cdot}150$
Specific heat of dry salt, ...	$s = 0{\cdot}278$
Specific heat of steam at constant pressure, .	$c = 0{\cdot}378$

These data give us the value of $T_2 = 439{\cdot}2$ approximately, or a fall of 45·2° in stage (4).

To calculate how much less than this the fall in temperature is on dissolving in the ordinary way, we require to make some estimate of the osmotic pressure as explained above. Assuming van't Hoff's law to hold in the case of solutions containing so large a quantity of the salt as that we are dealing with here, we have for the osmotic pressure at 121°, taking the density of the solution then to be 1·52, and that 215/315 of it is salt.

$$P = 3{\cdot}95 \times 10^8 \text{ dynes/sq. c.}$$

An estimate of the specific heat of the solution $S = {\cdot}66$ was graphically made by exterpolation from data given in Landholt and Bornstein's Tables for the specific heat of sodium nitrate solutions of different densities. From these we get, for that part of the fall in temperature due to work done in stage (4), the value 4·5°. On subtracting this from 45·2°, we finally get for the fall in temperature due to ordinary solution the value 41·7°. This result must not be taken for more than the degree of accuracy of the data on which it is based will warrant. Notably in the case of the value taken for the osmotic pressure* of the saturated solution there is necessarily great uncertainty; however a large error in this would not seriously affect the main conclusions arrived at.

* Assuming the correctness of the method, it affords a way of deducing from experiment a value for the osmotic pressure of extremely strong solutions so soon as sufficient data of the various quantities involved are accumulated.

PART III.

The Heat of Solution of Sodium Nitrate in Water at the boiling point of the Saturated Solution.

The determination of the heat absorbed in the solution of sodium nitrate in water was made by heating the water and salt separately to a sufficiently elevated temperature, then mixing them together and observing the consequent fall in temperature. The temperature to which they were raised was varied on trial with the object of arranging that, when the salt became completely dissolved, the resulting solution should be just at its boiling point under atmospheric pressure. The water and salt were taken in the proportion about 1 to 2·15 that in which they are present in the saturated solution, boiling at the ordinary pressure. They were heated in closed vessels, which could be thrown into communication by opening a tap for the purpose of letting them mix together.

Description of Apparatus.

The apparatus consisted essentially of two copper spheres connected together by a short tube, carrying a stop-cock, as shown in fig. 4. The upper sphere was made quite light, as it only had to carry the salt. A thermometer was inserted in it through the top. The lower sphere which was to hold the water had to be stronger, in order to stand the pressure of the steam. The tube connecting the spheres was prolonged inside the lower one to almost the bottom, so that, on turning on the tap, the pressure of the steam might drive the water up so as to mix with the salt in the upper sphere. The connecting-tube fitted into the spheres by means of screw junctions, and could thus be readily removed, leaving openings through which to introduce the water or salt.

Method of Procedure.

The apparatus having been charged in the proper proportions,* the whole was immersed in an oil bath until the temperature indicated by the

* The salt was powdered and sifted so as to be as fine as possible in order to facilitate rapid solution.

thermometer was the same as that of the oil bath. This took about five hours owing to the salt being such a poor conductor of heat. To prevent an increased air-pressure affecting the thermometer, the upper sphere was not screwed tight home till just the last, so as to let the air-bubble out as the heating proceeded.

Thermostat Employed.

Considerable difficulties were experienced at first in getting a thermostat capable of keeping the temperature of the oil bath sufficiently constant at the comparatively elevated temperatures necessary. The arrangement finally adopted consisted of a long glass tube, containing air, which passed up and down through the oil bath. One end of this tube was fitted with a short piece of rubber tubing, which could be closed with a pinch-cock on the desired temperature being reached. The other end of the glass tube joined into a bulb containing mercury. From the bottom of this bulb a tube leads, which turned upward, and bifurcated to form the cut-off valve for the coal gas going to supply the flame heating the oil bath. The amount of mercury introduced was such that gas entering by one limb could just pass freely out through the other, but should the pressure on the mercury in the bulb become increased, through the air in the long tube rising in temperature, the gas was partially cut off by the mercury rising and partially blocking the free passage at the bifurcation. This arrangement gave highly satisfactory results.

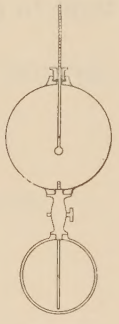

Fig. 4.

Making the Observations.

As mentioned before, it took some hours for the salt to reach the temperature of the oil-bath. This being accomplished, all was ready for observing the fall in temperature on mixing. The apparatus was then lifted half out of the oil bath, and the tap quickly turned on. The water below was then blown up, so as to mix with the salt in the upper sphere. Immediately the thermometer fell in consequence of the salt going into solution, and rapidly reaching the end of its sudden fall, paused and rose slightly, due, no doubt, to heat flowing in from the hot copper wall of the sphere, and, finally then, the cooling down of the whole, due to radiation, was seen to proceed.

Results obtained.

In Table V. are given the final results obtained with this apparatus for sodium nitrate and water. The salt and water were in the proportion of about 2·15 to 1, that of the saturated solution with the maximum boiling point at atmospheric pressure.

In the first columns is given the temperature before mixing; in the second that after. The true fall is probably slightly greater than that observed, the errors tending that way. Both the influx of heat from the wall of the sphere and any incomplete mixing of the salt with the water tend to give a diminished fall.

TABLE V.

θ_1	θ_2.	Fall.
157·0	116·0	41·0
159·5	119·5	40·0
160·5	120·0	40·5
161·0	122·0	39·0
161·5	121·5	40·0
Mean, . . .		40·1

This result is, within the errors of experiment, in agreement with the calculated value 41·7, given in Part II., and would seem therefore to afford a confirmation of the considerations there used in deducing the reversible cycle.

To make an estimate of the latent heat of solution of sodium nitrate and water, one can take the estimate for the value of the specific heat of the solution $S = \cdot 66$ given in Part II. In this way it is found that on 2·15 grams of salt going into solution in one of water at 160°, about 83 units of heat are absorbed.